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<b>(21) International Application Number:</b> PCT/FI98/00194 <b>(22) International Filing Date:</b> 4 March 1998 (04.03.98) <b>(30) Priority Data:</b> 970936 5 March 1997 (05.03.97) FI <b>(71) Applicant (for all designated States except US):</b> NESTE OY [FI/FI]; Keilaniemi, FIN-02150 Espoo (FI). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> PAVLYUCHENKO, Valery [RU/RU]; Energetikov pr., 66-1-205, St.Petersburg, 195253 (RU). BYRDINA, Nina [RU/RU]; Iskrovsky pr., 8-3-40, St.Petersburg, 193313 (RU). IVANCHEV, Sergey [RU/RU]; Nalichnaya ul., 36-3-97, St.Petersburg, 199266 (RU). SKRIFVARS, Mikael [FI/FI]; Katajahaantie 2 A 20, FIN-00200 Helsinki (FI). HALME, Erkki [FI/FI]; Kyläkunnantie 7, FIN-00660 Helsinki (FI). LAAMANEN, Hanna [FI/FI]; Kaivosmestarinkatu 3 D 56, FIN-02770 Espoo (FI). KOSKINEN, Jukka [FI/FI]; Westendintie 105, FIN-02160 Espoo (FI). <b>(74) Agent:</b> FORSSÉN & SALOMAA OY; Yrjönkatu 30, FIN-00100 Helsinki (FI).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> A METHOD FOR THE PREPARATION OF HOLLOW POLYMER PARTICLE LATEX		
<b>(57) Abstract</b> <p>The present invention is concerned with a method for the preparation of latexes with hollow polymer particles useful as opacifying agents. The process comprises the preparation of hollow polymer particle latex by emulsion copolymerization with water soluble initiator and anionic surfactant as follows: a) preparation of seed latex of copolymer containing methyl methacrylate and methacrylic acid; b) preparation of latex of highly carboxylated copolymer containing methyl methacrylate and a cross-linking agent and optionally a vinyl aromatic compound; c) using highly carboxylated latex synthesized at stage b) in the preparation of the intermediate shell comprising a copolymer of methyl methacrylate, acrylic acid ester, a cross-linking agent and optionally vinyl aromatic compound, said intermediate shell copolymer having a glass transition temperature below 80 °C; d) swelling the particles prepared at stage c) by addition of volatile basic compound; e) preparation of a hard shell on the swollen expanded particles comprising a copolymer of vinyl aromatic compound, acrylonitrile and/or methyl methacrylate, and cross-linking agent, said hard shell having a glass transition temperature above 80 °C; and f) optional preparation of an external shell.</p>		

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A method for the preparation of hollow polymer particle latex.

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The present invention relates to a method for the preparation of latexes with hollow polymer particles. Hollow polymer particles are useful as opacifying agents in coating applications such as in paint or paper coating, especially for high quality paper products where colour pictures are presented, such as art books, brochures, annual reports, magazines etc. The use of hollow particle latex in such coatings reduces or removes the need for pigments, such as titanium dioxide, or extenders, without adding excessive and undesirable weight to the coating. The hollow polymer particle latex provides opacity because the hollow structure in a latex particle scatters light more efficiently than a corresponding particle of uniform density. The light scattering properties are related to a difference in the refractive index between the shell and the internal void. The particles can also be used as control release devices for target compounds. Hollow polymer particles have found extensive applications as white pigments ie. hollow sphere pigments having excellent optical properties such as hiding power, opacity, gloss, brightness and whiteness as well as thermal resistance providing benefits in printing performance and production efficiency, for example faster calendering and they have started to replace the earlier used polymers filled uniformly in particles.

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In the prior art some methods have been known for the production of microvoid containing polymer particles. All these methods lead to a core and shell particles with different microvoids in the centre. The hollow polymer latex particles having a centered void have a greater utility in coatings than those structures having microvoid or hemispherical particles with voided centers.

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Some methods have also been proposed for the preparation of hollow polymer particles. *EP patent number 22633* discloses a process which comprises copolymerizing an ethylenically unsaturated monomer with a carboxyl group

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containing ethylenically unsaturated monomer by emulsion polymerization to prepare seed particles of the core part, carrying out cover polymerization using an ethylenically unsaturated monomer for the formation of the particle surface layer eg. shell part, neutralizing after completion of polymerization the resulting particles with a volatile base such as ammonia, and swelling the particles into hollow particles. In this process four-stage polymerization is carried out so as to make a polymer composition of the core part and the shell part different. The process is complicated and it is difficult to control the reaction temperature, the quantity of the polymerization initiator, the quantity of the surfactant etc and thus it is difficult to form hollow particles stably, resulting in leaving high levels of copolymerized acid in the core polymer. There also appears to be no intermediary layer between the core and the shell, which may be the reason for the weak opacity.

The *US patent No. 4,427,836* discloses the production of sequential heteropolymer dispersion and a particulate material obtainable therefrom, comprising an ionic, swellable, hard core polymer and a sheath polymer on the core. In this method the preparation of the core/sheath polymer particles is realized using sequential emulsion polymerization to yield the core, then polymerizing the sheath on the core particles, neutralizing the resultant core/sheath particles to swell the core and to form particles with a single void when dried. The product contains only two layers, the core and the sheath. This may be the reason why the opacifying compositions are only whitish but not white.

*US patent No. 4,880,842* discloses a process for making hollow latexes by introducing a non-polymeric acid to an early stage of the multi-stage polymer particles instead of copolymerizing acid to make swellable cores. This method for preparing hollow latexes requires cores containing acid or acidic monomers to enable swelling to occur at room temperature. The existence of acid in a polymer disadvantageously increases the polymers' affinity to water. The sensitivity to the effects of water undesirably renders the coating into which the latex is formulated, sensitive to moisture as well, which is an undesirable property in coating applications. An acidic core is also thought to impart polarity to the polymer and because of such polarity

the polymer is thought not to absorb surfactants well, rendering the polymer unstable or prone to coagulation or aggregation in larger particles. The water sensitivity of the core or high affinity for water by the core is thought to make it difficult to encapsulate the core with the shell polymer because the core tends to remain at the polymer-water interface on the surface of the particle rather than to be encapsulated by the shell. This process for preparing hollow polymer particles also requires a post-encapsulating step with cross-linked polymers, that is the acid containing cores are encapsulated with an uncross-linked shell, the core is swelled and then the shell can be encapsulated with cross-linked polymers. Additionally substantive amounts of the chain-transfer agent n-dodecyl mercaptan are needed to accomplish this process.

The *US patent No. 4,910,229* discloses a process which comprises adding a base to a carboxyl group containing copolymer latex to neutralize at least part of the carboxyl groups in the copolymer, eg. base treatment and then lower the pH of the latex with an acid, eg. acid treatment to produce hollow particles. In this process it is necessary to neutralize the carboxyl groups in the polymer particles, and in order to make the base necessary for neutralization permeate sufficiently into the polymer particles, there is a necessity to raise treatment temperature from a temperature somewhat lower than the glass transition temperature ( $T_g$ ) of the polymer to a temperature equal to or more than  $T_g$  and raise the diffusion rate of the base. Usually this kind of process results in multihollow morphology of the particles.

*US patent No. 5,360,827* discloses a process for the preparation of latex of a hollow polymer which comprises adding a base in the presence of a monomer to latex containing carboxylic modified copolymer particles to make the pH of the latex 8 or more, and adding a carboxyl group containing a monomer to make pH of the latex 7 or less and then polymerizing these monomers. This process leaves high amounts of residual monomers in the product and thus an additional steam distillation operation is required.

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*US patent No. 5,157,084* discloses a process of making hollow polymer latex particles without the use of acid in the swellable polymer core. The swelling step is

performed at elevated temperatures, usually above 100°C and thus it must be performed under pressure.

5 The *European patent application, publication No. 478 829* discloses a process for the preparation of hollow latex polymers characterized by emulsion polymerization of monomers in the presence of organic hydrocarbons, which tend to leave solvent residues in the product and are costly to use. An additional operation is needed for the removal of residual solvents from the product.

10 In general, all methods of the state of art are multistage processes requiring the isolation of the intermediate latexes, several reactors and time consuming expensive cleaning operations between the stages.

15 An object of the present invention lies in providing a new, efficient, economic and environmentally advantageous process for the preparation of stable hollow polymer latex particles, based on the development of a hard, cross-linked shell on highly carboxylated seed particles pre-swelled in aqueous volatile base solution. Surprisingly the present inventors found that the above-identified objects can be attained by realizing the following process, which requires no chain transfer agents, no additional steam distillation steps, no pressurizing, no organic solvents, no elevated  
20 temperatures above 100°C and which yields a white and opaque product with an additional intermediary layer. The process can be performed batchwise in one reactor without any isolation of intermediate latexes and without additional cleaning etc. operations.

25

Accordingly, the present invention provides for an efficient and economic process for the preparation of hollow latex polymer particles with high glass transition temperature  $T_g$ , with particle size between 0.3—0.6  $\mu\text{m}$  and with suitable rheology.

30 The process comprises preparing hollow polymer particle latex by emulsion copolymerization with water soluble initiator and anionic surfactant, using batch, semi-continuous batch or continuous batch methods as follows:

- a) preparation of seed latex of copolymer containing methyl methacrylate and methacrylic acid;
- b) preparation of latex of highly carboxylated copolymer containing methyl methacrylate and a cross-linking agent and optionally a vinyl aromatic compound;
- c) using highly carboxylated latex synthesized at stage b) in the preparation of the intermediate shell comprising a copolymer of methyl methacrylate, acrylic acid ester, a cross-linking agent and optionally vinyl aromatic compound, said intermediate shell copolymer having a glass transition temperature below 80°C;
- d) swelling the particles prepared at stage c) by addition of volatile basic compound;
- e) preparation of a hard shell on the swollen expanded particles comprising a copolymer of vinyl aromatic compound, acrylonitrile and/or methyl methacrylate, and cross-linking agent, said hard shell having a glass transition temperature above 80°C; and
- f) optional preparation of an external shell consisting of a copolymer of vinyl aromatic compound, acrylic acid ester, methacrylic acid and a cross-linking agent with glass transition temperature below 15°C.

Stage a) preferably comprises the preparation of a seed latex copolymer containing methyl methacrylate and methacrylic acid and the optional preparation of the seed latex when weight ratio of monomer/initiator/water is equal to  $1/(0.1-0.3)/(50-150)$ .

The ratios of the weight concentrations of the copolymers prepared during different stages are important parameters of the process.

Preferred ratios of the polymers obtained in different stages are presented below.

6

Stage No	a	b	c	e	f
Preferred					
ratio	1	5—20	25—60	20—60	2—60

- 5 The overall process is preferably performed in a single reactor as a one-pot process but it also may be performed as a conventional stepwise process with the isolation of intermediate latexes using several reactors.

10 At stage a) seed latex is prepared by emulsion copolymerization of 98.8—99.5 weight parts, preferably 97.0—98.5 weight parts of methyl methacrylate with 0.5—4.0 weight parts, preferably 1.5—3.0 weight parts of methacrylic acid.

15 When preparing the hollow latex polymer particle via a seeded process, a seed latex prepared at stage (a) having a particle size from 70 to 180 nm is required, and the particle size range of 80—130 nm is preferred.

20 At stage b) latex of highly carboxylated copolymer containing methyl methacrylate, cross-linking agent and acid monomer is prepared by using the seed latex prepared at stage a) for obtaining copolymer latex.

25 The preferred acid monomers that may be used for the alkali-swellable core are monoethylenically unsaturated carboxylic acid monomers, such as, acrylic acid, methacrylic acid and itaconic acid. As the principal role of the acid monomers at stages a), b), and c) the acid monomers provide the preparation of the carboxylated core, which is able to swell when the carboxylic groups are neutralized with a volatile base, at stage f) the acid monomers primarily provide the stability of the latex.

30 The cross-linking agent is meant to include monomers conventionally known in the art as useful for cross-linking polymerizable monomers. Examples of such monomers typically include di- or trifunctional monomer such as divinyl benzene, ethylene glycol methacrylate, ethylene glycol acrylate and allyl methacrylate.



In the copolymerization of core polymer latex 60—80 parts, preferably 65—75 parts of methyl methacrylate and 20-40 parts, preferably 25—35 parts of acid monomer, and 0.3—0.8 parts, preferably 0.4—0.6 parts of cross-linking agent are used.

- 5 The acid monomers provide the preparation of carboxylated core which is able to swell when the carboxylic groups are neutralized at later stage (d) with volatile base. In addition, the acid monomers improve the colloidal stability of the latexes, especially at stage f).
- 10 At stage c) the highly carboxylated latex prepared at stage b) is used for the preparation of an intermediate shell on latex particles. The intermediate shell comprises a copolymer of methyl methacrylate, acrylic acid ester and cross-linking agent and said intermediate shell has a glass transition temperature below 80°C. The acrylic acid ester may be, for example, n-butylacrylate, isobutyl acrylate or 2-ethyl hexyl-
- 15 acrylate.

- The amount of monomers used at stage c) are as follows: 60—85 weight parts, preferably 70—80 weight parts of methyl methacrylate, 15—25 weight parts, preferably 16—19 weight parts of acrylic acid esters and 2—8 weight parts, preferably
- 20 ably 4—5 weight parts of acid monomers. Optionally the monomer mixture contains also 0—0.6, preferably 0.1—0.3 weight parts of cross-linking agents mentioned above.

- At stage d) the particles prepared at stage c) are swelled by adding a volatile basic
- 25 compound.

Volatile bases, such as, ammonia or volatile organic bases, such as, triethylamine, trimethylamine or diethyl ethanol amine are used as suitable swelling agents.

- 30 The concentration of volatile basic compound at stage (d) is preferably calculated in accordance with the following equation:

$$[B] = a/D - b$$

where [B] is the volatile base concentration calculated as milliequivalents per 1 g of methacrylic acid charged at stages (a), (b) and (c), D is number average diameter of the seed particles (in nanometers) prepared at stage (a) and a and b are constants, ie.  
5 a = 1670 and b = 4.1.

The volatile base concentration at stage (d) is preferably 2—10% by weight and more preferably 3.5—6% by weight.

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The swelling time can be 30—120 min, preferably 40—80 min.

At stage e) a hard shell having a glass transition temperature above 80°C is prepared on the swollen expanded particles from stage c). This shell comprises a copolymer  
15 of vinyl aromatic compound, such like styrene, acrylonitrile and/or methyl methacrylate and a cross-linking agent. The monomers used at this stage are as follows: 0—35 weight parts, preferably 15—30 weight parts of methyl methacrylate, 60—99 weight parts, preferably 70—80 weight parts of styrene, 0—35 weight parts, preferably 15—30 weight parts of acrylonitrile and 1—10 weight parts, preferably  
20 2—5 weight parts of cross-linking agent mentioned above.

An optional stage f) comprises preparation of an extended shell consisting of a copolymer of vinyl aromatic compound, an acrylic acid ester, methacrylic acid and a cross-linking agent and having a glass transition temperature below 15°C. This can  
25 be obtained by copolymerizing 3—10 weight parts, preferably 4—7 weight parts of methacrylic acid, 55—75 weight parts, preferably 60—75 weight parts of acrylic acid ester, 20—40 weight parts, preferably 30—35 weight parts of styrene and 0.2—3.5 weight parts, preferably 0.4—1.0 weight parts of cross-linking agent.

30 Vinyl aromatic compounds, such like styrene, p-methylstyrene and mixtures of isomers of methylstyrene can optionally be used at stages b) and c). The amount of vinyl aromatic compound is 0—20 weight parts, preferably 0—10 weight parts.

Further the ratio of weight concentrations of the sum of methyl methacrylate and vinyl aromatic compound to acrylic acid ester at stage c) is preferably within the range of 3.3—4.3 and the ratio of weight concentration of the copolymer prepared at stage (f) to the copolymer prepared at stage (e) is preferably 0.1—1.0.

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The overall reaction temperature at all stages except stage (d) is 60—95°C, preferably 80—90°C. The reaction temperature of stage (d) is 80—95°C.

10 The water soluble free radical initiators suitably employable in the aqueous phase are those typically known in the art, for example sodium persulphate, potassium persulphate and ammonium persulphate. The effective amount of the initiator can be from 0.25 to about 3.00%, preferably 0.6—1.45% by weight of the monomer charged at all stages. The initiator is added at stage b) advantageously as two equal portions in the beginning of the reaction and in the middle of the reaction.

15

In all steps surface active agents typically known in the art for polymerization processes can be used. Typical surfactants include anionic emulsifiers, such as, sodium dodecyl benzene sulphonates, sodium alkyl sulphonates ( $C_{12}$ — $C_{18}$ ) in effective amounts to assist in stabilizing the particle as a colloid minimizing contact  
20 between the particles and preventing coagulation, when used before the swelling step.

A higher polymer solid level will increase the need for surfactant. An effective amount of the surfactant can be 0.1—3% by weight of the monomer charged, in  
25 some cases no surfactant is needed. Advantageously the anionic surfactant is charged as equal portions in equal periods of time.

The obtained final product contains very low concentrations of residual monomers, which is due to the reaction conditions of this process.

30

The hiding power of hollow particle polymer latexes is determined by the following method. The hiding power can be expressed by the amount of grams of the pigment

for a surface of 1 m<sup>2</sup> using a photometric method. 4 to 5 glass plates are coated with a latex composition (hollow particles + film forming latex). The reflection coefficient of the coated glass plate at  $\lambda = 582$  nm is determined using a photometer. The glass plate is placed on a white surface with the reflection coefficient of 86% and  
 5 then on black surface with reflection coefficient of less than 1%. Then the contrast coefficient R is calculated as the ratio of reflection coefficients. Hiding power is calculated from the relation of R and weight content of the pigment for a surface of 1 m<sup>2</sup>. Weight content of the pigment (PWC) value relevant to  $R = 0.98$  is taken for hiding power.

10

The diameter of the hollow particle is determined experimentally as well as the wall thickness.

The hollow polymer particle latexes of the present invention may be used in coating  
 15 formulations or coating systems to replace all or part of opacifying pigments.

The hollow polymer particle latex may be formulated to a composition for the preparation of white and opaque coatings, for example, in the following manner:

20	Hollow particle latex with solids 28—32%	4.5—5.0 g
	Film forming latex (latex of copolymer of styrene-acrylic acid ester-acrylic acid) with minimum film formation temperature from 10—15°C, with particle size 200—300 $\mu$ m	7.5 g
25	Water	2.0 to 4 g
	Ammonia solution (7.2 %)	0.2—0.3 g

The following examples are illustrative embodiments of the present invention and are not meant to narrow the scope of the process of the invention.

30

**Example 1**

The process is carried out in a 200 cm<sup>3</sup> reactor equipped with anchor type stirrer, reflux condenser, nozzle for the inert gas input and the device for monomer feeding  
5 at 80°C under constant values of stirring and nitrogen flow.

Stage (a): 0.0018 g of sodium dodecylbenzene sulfonate (SDBS) dissolved in 49.9 g of water is charged into the reactor and the nozzle for gas is connected. SDBS solution is heated to 80°C for 30 min. Then 0.092 g of potassium persulfate (PP)  
10 dissolved in 6.3 g of water is charged. Within 15 min. monomer mixture consisting of 0.453 g methyl methacrylate (MMA) and of 0.0088 g methacrylic acid (MAA) is charged. The process continues after charging for 1 hour and results in the formation of latex with 100 nm particle size containing 1.18% solids.

15 Stage (b): 0.0046 g of SDBS dissolved in 2.3 g of water is charged into the reactor containing the whole amount of the latex prepared at stage (a). In 10 minutes feeding of the monomer mixture consisting of 3.624 g MMA, 1.502 g MAA and 0.031 g ethylene glycol dimethacrylate (EGDM) is started it is and then continued for 3 hours with constant rate followed by the process for half an hour.

20

Stage (c): Aqueous solution of SDBS and 0.101 g of PP dissolved in 7.43 g water is added to the latex prepared at stage (b). In 10 minutes feeding of monomer mixture consisting of 12.002 MMA, 2.806 g n-butyl acrylate (BA), 0.709 g MAA, 0.026 g EGDM is started and then continued for 4.5 hours with constant rate. Then  
25 the process is continued for half an hour.

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SDBS solution (0.227 g in 8.00 g of water) is charged by 4 equal portions. The first portion is charged at the beginning of stage (c) and every next portion is charged in 70 minutes from the beginning of the previous charge.

Stage (d): 11.90 g of 4.0% aqueous ammonia solution is charged into the latex prepared at the stage (c) for 40 minutes.

Stage (e): 0.270 g of PP dissolved in 16.1 g of water is charged into the latex neutralized by ammonia. In 10 minutes the feeding of the monomer mixture containing 11.40 g styrene (ST), 3.84 g MMA, 0.27 g divinyl benzene (DVB) is started and completed within 3 hours. Then the process is continued for half an hour with subsequent cooling of the reaction mixture to 30—40°C and the latex obtained is collected.

Characteristics of the latex prepared:

	Solids	26.2% wt
10	Particle diameter	370 nm
	Hollow diameter	270 nm
	Residual monomers	
	Styrene	0.03 % wt
	n-Butylacrylate	0.04 % wt
15	Methylmethacrylate	0.007 % wt

The characteristics of the coating based on hollow particle latex and film forming latex (ST:BA:glycidil methacrylate:MAA = 26.7:57.5:10.0:5.8% wt):

20 Hiding power of the coating: 60.5 g of hollow pigment/m<sup>2</sup>.

**Example 2**

The process is carried out in 350 cm<sup>3</sup> reactor equipped with anchor type stirrer, reflux condenser, nozzle for the inert gas input and the device for monomer feeding at 80°C under constant values of stirring and nitrogen flow.

30 Stage (a): 0.031 g of SDBS dissolved in 120 g of water is charged into the reactor and the nozzle for gas is connected. SDBS solution is heated to 80°C for 30 minutes. Then monomer mixture consisting of 14.82 g MMA and 0.28 g MAA is charged. Within 10 min 0.134 g of PP dissolved in 15 g of water is charged. The

process continues after charging for 7 hours and results in the formation of latex with 90 nm particle size containing 9.70% wt of solids.

5 Stage (b): 10.11 g of seed latex prepared at stage (a) containing 80.4 g of water is charged into the reactor, stirring is started and the nozzle for gas is connected. Seed latex is heated to 80°C for 40 min. Then 0.045 g of PP dissolved in 25 g of water is added to the latex and in 10 minutes feeding with monomer mixture containing 6.74 g MMA, 2.84 g MAA. 0.06 g EGDM is started. In 2.5 hours from the beginning of the process 0.045 g of PP dissolved in 2.5 g of water is charged  
10 additionally. Feeding continues for 5 hours followed by the process for another 1.5 hours.

Stage (c): Aqueous solution of SDBS and 0.22 g of PP dissolved in 6.45 g of water is added to the latex prepared at the stage (b). In 10 minutes feeding of the monomer  
15 mixture consisting of 23.88 g MMA, 5.68 g BA, 1.42 g MAA, 0.043 g EGDM is started and then lasts for 4.5 hours with constant rate. Then the process is continued for another hour.

20 SDBS solution containing 0.48 g in 8 g of water is charged by 4 equal portions. The first portion is charged at the beginning of the stage (c) and every next portion is charged in 70 min from the beginning of the previous charge.

Stage (d): 29.4 g of 3.6% aqueous solution of ammonia is charged into the latex prepared at the stage (c) for 40 minutes.

25 Stage (e): 0.39 g of PP dissolved in 20.15 g of water is charged into the latex neutralized by ammonia. In 10 minutes the feeding of the monomer mixture containing 18.86 g ST, 6.48 g acrylonitrile (AN) and 0.48 g DVB is started and completed within 3 hours. Then the process is continued for 1.5 hours with subsequent cooling  
30 of the reaction mixture to 30—40°C and the latex obtained is collected.

Stage (f): 15.4 g of 3.5% aqueous solution of ammonia is charged into the latex prepared at the stage (e) for 15 min at 80°C. Then 0.28 g of SDBS and 0.36 g of PP dissolved in 28.5 g of water is added. In 10 minutes the monomer mixture containing 3.82 g ST, 6.74 g BA, 0.57 g MMA, 0.23 g EGDM is added. After the charging is completed the process continues for 40 min. The latex is cooled and collected.

Characteristics of the latex prepared:

10	Solids	27.62 % wt
	Particle diameter	430 nm.
	Hollow diameter	280 nm.
	Residual monomers	
	Styrene	0.006 % wt
15	n-Butylacrylate	0.024 % wt
	Hiding power of the coating:	76.1 g of hollow pigment/m <sup>2</sup> .

### Example 3

20 The process is carried out according to that described in Example 2 with the following differences and additions:

Stage (a) recipe:

	MMA	14.82 g
25	MAA	0.28 g
	SDBS	0.02 g
	PP	0.134 g
	Water	135 g
	Solids	9.76% wt
30	Particle diameter	100 nm



SDBS dissolved in 1 g of water is charged in the beginning of the process.

Stage (c)

Recipe

5 Latex prepared at stage (b)

MMA 18.43 g

ST 4.60 g

BA 5.26 g

MAA 1.36 g

10 EGDM 0.05 g

SDBS 0.43 g

PP 0.19 g

Water 15.6 g

15 Stage (d)

Recipe

Latex prepared at stage (c)

Ammonia 3,5% wt aqueous solution 21.9 g

20 Stage (e)

Recipe

Latex prepared at stage (d)

ST 28.17 g

MMA 9.41 g

25 DVB 0.76 g

PP 0.74 g

Water 75.0 g

16

Stage (f)

Recipe

Latex prepared at stage (e)

	ST	1.39 g
5	BA	2.45 g
	MAA	0.21 g
	EGDM	0.05 g
	Ammonia 3.5% wt aqueous solution	5.6 g
	SDBS	0.10 g
10	PP	0.13 g
	Water	10.4 g

Characteristics of the latex prepared

	Solids	33.9% wt
15	Particle diameter	560 nm
	Hollow diameter	310 nm
	Hiding power of the coating: 71.1 g of hollow pigment/m <sup>2</sup>	
	Residual monomers: Methyl methacrylate 0.010% wt, n-Butylacrylate 0.012% wt, Styrene 0.0333% wt.	

20

**Example 4**

The process is carried out according to that described in Example 2 with the following differences and additions.

25

Stage (a) is carried out according to Example 3.

Stage (b):

Recipe

30	Seed latex	11.33 g
	MMA	7.56 g
	MAA	3.18 g

EGDM 0.07 g

PP 0.11 g

Water 101.5 g

Feeding lasts for 7 hours followed by the process for another 1 hour.

5

Stage (c):

Recipe

Latex prepared at stage (b)

MMA 29.37 g

10 BA 6.77 g

MAA 1.74 g

EGDM 0.07 g

PP 0.26 g

SDBS 0.55 g

15 Water 21.46 g

Stage (d): 27.8 g of ammonia 3.8% aqueous solution is charged.

Stage (e):

20 Recipe

Latex prepared at stage (d)

ST 25.85 g

AN 8.50 g

DVB 1.39 g

25 PP 0.69 g

Water 21.86 g

Characteristics of the latex prepared:

Solids 25.5% wt.

30 Particle diameter 500 nm

Hollow diameter 300 nm

Residual monomers

18

Styrene                    0.04 % wt  
Divinylbenzene        0.003 % wt

Hiding power: 75.4 g of hollow pigment/m<sup>2</sup>

5

### Example 5

The process is carried out according to that described in Example 4 with the following differences and additions:

10

Stage (a)

Recipe

MMA                    14.84 g

MAA                    0.28 g

15 

SDBS                    0.016 g

PP                      0.134 g

Water                   135 g

Particle diameter 120 nm

20 

Stage (d): 22.5 g of ammonia 3.8% aqueous solution is charged.

Characteristics of the latex prepared:

Solids                    26.8% wt

Particle diameter       500 nm

25 

Hollow diameter       370 nm

Residual monomers:

Styrene                   0.04 % wt

Divinylbenzene        0.003 % wt

Hiding power: 66.7 g of hollow pigment/m<sup>2</sup>

30

**Example 6**

The process is carried out according to that described in Example 4 with the following differences:

5

Stage (a) is carried out according to Example 2.

Stage (b):

Recipe

10	Seed latex	8.60 g
	MMA	7.82 g
	MAA	2.54 g
	EGDM	0.051 g
	PP	0.084 g
15	SDBS	0.006 g
	Water	60.8 g

Stage (c)

Recipe

20	Latex prepared at stage (b)	
	MMA	26.72 g
	BA	6.10 g
	MAA	1.57 g
	EGDM	0.06 g
25	SDBS	0.50 g
	PP	0.22 g
	Water	18.0 g

Stage (d)

30 Recipe

Latex prepared at stage (c)

23.7 g of ammonia 3.8% aqueous solution

## Stage (e)

## Recipe

Latex prepared at stage (d)

	ST	32.68 g
5	MMA	10.91 g
	DVB	0.35 g
	PP	0.86 g
	Water	76.2 g

## 10 Characteristics of the latex prepared:

Solids	33.9%
Particle diameter	560 nm
Hollow diameter	280 nm

Residual monomers

15	Styrene	0.03 % wt
	n-Butylacrylate	0.018 % wt
	Methylmethacrylate	0.013 % wt
	Hiding power:	76.0 g of hollow pigment/m <sup>2</sup>

## 20 Comparative example.

Preparation of latex according to US Patent 4,427,836

The preparation of seed latex.

25

The process is carried out in a 500 cm<sup>3</sup> flask equipped with a stirrer, reflux condenser, nozzle for the inert gas input and device for feeding monomers. Distilled water 290 g and 0.20 g of SDBS are heated in the flask to 78°C under nitrogen atmosphere with stirring. The monomer emulsion is prepared using 27 g of water, 0.04 g of SDBS, 41.6 g of BA, 37.4 g of MMA and 1.04 g of MAA. 5 g of the emulsion is added to the flask. Then 0.3 g of ammonium persulfate is dissolved in 1 ml of water. In 15 minutes the feeding of the remaining monomer emulsion is started with

the rate of 1.6 g/min. 15 min after the monomer feeding is completed the reaction mixture is cooled. Then 0.14 cm<sup>3</sup> of t-butyl hydroperoxide (50%) and 0.05 g of sodium formaldehyde sulfoxylate dissolved in 2 cm<sup>3</sup> of water are added at 55°C. Then 1.16 g of 24% aqueous solution of ammonia is added at 25°C.

5

**Stage A.**

0.42 g of sodium persulfate (SP) dissolved in 2.5 g of water is added to 211.5 g of water heated to 84°C in the 500 cm<sup>3</sup> flask under nitrogen atmosphere followed by  
10 the addition of 6.2 g of seed latex. A monomer emulsion consisting of 23.5 g of water, 0.08 g of SDBS, 49 g of MMA, 21 g of MAA and 0.35 g of ethylene glycol diacrylate is added to the flask at 85°C over 3 hour period. After the completion of the monomer feeding the dispersion is held at 85°C for 30 min and cooled to 25°C.

15 **Stage B.**

0.21 g of SP followed by 13.5 g of latex obtained at Stage A are added to 240 g of water heated to 85°C in a stirred reaction flask. 54 g of MMA is added over 1 hour period at 85°C. The temperature is maintained at 85°C for another 1.5 hours. Then  
20 a monomer mixture consisting of 30 g of BA and 24 g of MMA is charged during 1 hour. The heating is continued for another 2 hours. Then the latex is cooled to 25°C.

**Stage C.**

25

Latex obtained at the Stage B is neutralized with 17.4 g of 10% aqueous solution of ammonia at 25°C under stirring. The neutralized latex is heated at 95°C for 1 hour and then cooled to 25°C.

30 The latex prepared is film forming at ambient temperatures. Therefore the hiding power measurements were carried out without addition of film forming latex. It appeared to be difficult to measure the hiding power using our techniques because

the contrast ratio (R) was too low even for thick coatings. For example, R is equal to 0.547 at 350 g/m<sup>2</sup> surface density of polymer pigment.



## Claims

1. A process for preparation of hollow polymer particle latexes by emulsion copolymerization with water soluble initiator and anionic surfactant, **characterized**  
5 in the following stages:
- a) preparation of seed latex of copolymer containing methyl methacrylate and methacrylic acid;
- 10 b) preparation of latex of highly carboxylated copolymer containing methyl methacrylate, monoethylenically unsaturated carboxylic acid and cross-linking agent and optionally a vinyl aromatic compounds, by using seed latex prepared in stage a);
- 15 c) using highly carboxylated latex synthesized at stage b) in the preparation of the intermediate shell comprising a copolymer of methyl methacrylate, acrylic acid ester, monoethylenically unsaturated carboxylic acid and cross-linking agent and optionally vinyl aromatic compound, said intermediate shell copolymer having a glass transition temperature below 80°C;
- 20 d) swelling the particles prepared at stage c) by addition of volatile basic compound;
- e) preparation of a hard shell on the swollen expanded particles comprising a copolymer of vinyl aromatic compound, acrylonitrile and/or methyl methacrylate, and cross-linking agent, said hard shell having a glass transition temperature above  
25 80°C; and
- f) optional preparation of an external shell.
2. Process according to claim 1, **characterized** in that the monoethylenically  
30 unsaturated carboxylic acid is methacrylic acid.

3. Process according to claim 1 or 2, **characterized** in that the seed latex prepared at stage (a) has particle size of from 70 to 180 nm.
4. Process according to any of claims 1—3, **characterized** in that stage b) comprises charging the water soluble initiator as two equal portions in the beginning of the reaction and in the middle of the process.
5. Process according to any of claims 1—4, **characterized** in that stage c) comprises charging the anionic surfactant as equal portions in equal periods of time.
6. Process according to any of claims 1—5, **characterized** in that the ratio of weight concentrations of the sum of methyl methacrylate and vinyl aromatic compound to acrylic acid ester at stage c) is within the range of 3.3—4.3.
7. Process according to any of claims 1—6, **characterized** in that the concentration of volatile basic compound at stage (d) is calculated in accordance with the following equation:

$$[B] = a/D - b$$

where [B] is the volatile base concentration calculated as milliequivalents per 1 g of methacrylic acid charged at stages (a), (b) and (c), D is number average diameter of the seed particles (in nanometers) prepared at stage (a) and a and b are constants, a = 1670, b = 4.1.

8. Process according to any of claims 1—7, **characterized** in that additionally after stage (e) stage (f) is performed, comprising preparation of an external shell consisting of a copolymer of vinyl aromatic compound, acrylic acid ester, methacrylic acid and a cross-linking agent with glass transition temperature below 15°C.

9. Process according to claim 8, **characterized** in that the volatile base concentration at stage (f) is equal to 20—80 meq per 1 g of methacrylic acid charged at stage (f).
- 5 10. Process according to claim 8 or 9, **characterized** in that the ratio of weight of the copolymer prepared at stage (f) to the copolymer prepared at stage (e) is 0.1—1.0.
- 10 11. Process according to any of claims 1—10, **characterized** in that the temperature of reaction is 60—95°C.
- 15 12. Process according to any of claims 1—11, **characterized** in that the process is performed in one reactor without isolation of intermediate products or it is performed stagewise with the isolation of intermediate products, in more than one reactors.
- 20 13. Process according to any of claims 1—12, **characterized** in that stage a) comprises the preparation of a seed latex of copolymer containing methyl methacrylate acid methacrylic acid; optional preparation of seed latex when weight ratio of monomers/initiator/water is equal to 1/(0.1—0.3)/50—150).
14. A coating formulation, **characterized** in that it comprises copolymer prepared according to any of claims 1—13.

1  
INTERNATIONAL SEARCH REPORT

International application No.  
PCT/FI 98/00194

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC6: C08F 285/00, C08F 265/06, C08F 2/22  
According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Polym. Mater. Sci.Eng., Volume 64, 1991, (Washington), J. W. Vanderhoff et al, "Preparation of soft hydrophilic polymer core/hard hydrophobic polymer shell particles for microvoid coatings by seeded emulsion polymerization", page 345 - page 346, & CA 115:159942  --	1-14
A	US 5360827 A (HEIDEKI TODA ET AL), 1 November 1994 (01.11.94), claim 1; column 2, line 34 - column 5, line 68  --	1-14
A	US 5521253 A (DO I. LEE ET AL), 28 May 1996 (28.05.96), claim 6  --	1-14

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document but published on or after the international filing date	"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

12 June 1998

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00194

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5157084 A (DO I. LEE ET AL), 20 October 1992 (20.10.92), claim 1  -----	1-14

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.

PCT/FI 98/00194

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US 5521253 A	28/05/96	AU 666332 B AU 2506692 A BR 9207160 A CA 2140035 A EP 0656033 A,B SE 0656033 T3 FI 950733 A JP 8500621 T WO 9404603 A US 5157084 A DE 69219904 D,T	08/02/96 15/03/94 31/10/95 03/03/94 07/06/95 17/02/95 23/01/96 03/03/94 20/10/92 11/12/97
US 5157084 A	20/10/92	US 5521253 A	28/05/96